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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application]This invention relates to an application type electrode of the monotonous type used for a storage battery, especially an alkaline battery, and a manufacturing method for the same.

[0002]

[Description of the Prior Art]There is a nickel electrode in the typical anode for alkaline batteries. This electrode is divided roughly and classified into a sintering type electrode and a non-sintering electrode. The former uses nickel nitrate solution etc. for the microporous sintered carrier produced by sintering nickel powder, adds nickel salt by dip coating, by being immersed after desiccation and into caustic alkali solution, converts said nickel salt into nickel hydroxide, and obtains a polar plate. This method has a complicated process and the pack density of nickel hydroxide which is an active material has a fault which becomes small compared with the non-sintering electrode described later. However, there is the feature excellent in the high rate discharging characteristic of an electrode, the cycle life, etc., and it is widely put in practical use according to the use. There is an electrode process called a pocket type in ancient times as a non-sintering electrode on the other hand, and the method of filling up with these days directly the nickel hydroxide powder which is active material powder into the letter nickel porous body of foaming has been put in practical use. Among these, according to the latter method, the process of an electrode can be simplified, since the letter nickel porous body of foaming of the degree of Ko Kota is possible, high-density restoration can be performed and there is the feature which can constitute the cell of high capacity. However, the letter nickel porous body of foaming is produced by electroplating, a nickel powder sintering process, etc.

There is a fault which the material cost attaches highly.

[0003]Therefore, development of the non-sintering electrode which uses a cheap punching metal, an expanded metal, etc. instead of the letter nickel porous body of foaming as electrode support has come to be carried out. For example, generally an expanded metal, the foil of nickel, a punching metal, etc. are used for the core material for electrodes (JP,S58-163157,A). Since it does not have a three-dimensional structure like a sintering type board and the letter nickel porous body of foaming, such electrode support is deficient in the holding power of an active material, when it is used as an electrode, and when under electrode production or charge and discharge is repeated, it tends to produce omission of an active material. Since the electron conductivity over the thickness direction of an electrode is scarce and the fall of an electrode characteristic is large, it is not put in practical use other than some electrodes.

[0004]Then, in order to enlarge surface area of electrode support and to reinforce the holding power of an active material, the conductive-electrodes base material (metal core object) which carried out blast processing of the surface of a nickel board and a nickel plate board, and was made into the split face is also proposed for many years (JP,S49-77142,A). The nonporous portion of the surface of the metal core object (punching metal) of a polar plate also has a proposal which provides a 10-100-micrometer burr shape projection (edged tool-like crack) (JP,58-41975,U). Using for an electrode the metal core material which formed conductive projections (powder, fibrous) by thermal spraying on the wire gauze, the punching metal, and a plate-like conductive porous body like a madreporite for the still more nearly same purpose is also proposed (JP,H1-302668,A).

[0005]

[Problem(s) to be Solved by the Invention]The electrode process which uses the punching metal mentioned above, an expanded metal, etc. as electrode support has the strong point which can produce an electrode easily by plastering the above-mentioned electrode support with active material powder as paste state with the solution and conductive powder of a macromolecular binding agent, and drying. However, the adhesion of the metal porous body and active material layer which are electrode support is weak, and when it uses as an electrode for cells, a metal porous body and an active material exfoliate easily. As a result, when electrode support serves as the charge collector, the electrical resistance of an electrode becomes large and causes a fall of discharge voltage and service capacity. In order to solve this problem, if a lot of binders are added in an active material layer, an exfoliation phenomenon will be controlled, but the reactivity of an active material falls and it has an adverse effect on a discharge characteristic.

[0006]In order to strengthen adhesion of a metal porous body and an active material layer, after making the layer of the thermoplastics which carries out the role of adhesives form in the metal porous body surface and making an active material form in the upper levels, there is also

a method of improving the adhesion of a metal porous body and an active material layer by heating. However, an insulating layer will be formed between a metal porous body and an active material layer, the current collection nature of an electrode falls, and the reactivity of an electrode is checked.

[0007]As mentioned above, when a comparatively planate metal porous body was used for electrode support, solution of said SUBJECT was difficult.

[0008]Therefore, this invention improves the application type electrode which plasters a metal porous body with active material powder, and an object of this invention is to improve the endurance of an electrode with the adhesion and electron conductivity of an active material layer and a metal porous body.

[0009]An object of this invention is to provide the improved application type electrode for cells applicable not only to a nickel electrode, a zinc electrode, and a cadmium electrode but the hydrogen storing metal alloy electrode which uses hydrogen storing metal alloy powder again, and its manufacturing method.

[0010]

[Means for Solving the Problem]An application type electrode for cells of this invention consists of a metal porous body and an application layer of an active material or hydrogen storing metal alloy powder formed in the both sides, and said metal porous body, punching a metal plate or a metallic foil from the both-sides side -- the punched hole -- it being formed in corrugated form of a barricade formed in the circumference, and, A non-punch station or an application-of-pressure punching portion for current collection is provided in a peripheral part of a metal porous body punched at said corrugated form in parallel to the undulating direction, and an electrode is constituted.

[0011]a hole by which a manufacturing method of an application type electrode for cells of this invention was punched at said corrugated form -- around a barricade, [have and] And it has a process made to plaster with a process, an active material, or hydrogen storing metal alloy powder conveyed to a parallel direction or rectangular directions to an undulating direction of a metal porous body band-like [long] which has a non-punch station or an application-of-pressure punch station around.

[0012]a hole by which a manufacturing method of an application type electrode for cells of this invention was punched at said corrugated form -- around a barricade, [have and] And an application layer which consists of an active material or hydrogen storing metal alloy powder is provided in metal porous body both sides constituted the long band-like one or the shape of short length which has a non-punch station or an application-of-pressure punch station around, and it has rectangular directions or the process of performing 1 times or more of a roller press in parallel, to an undulating direction of this metal porous body.

[0013]

[Function]By making the circumference of a hole generate a barricade in corrugated form at the time of punching, and using the corrugated form metal porous body which processed a planate metal plate or metallic foil in three dimensions as electrode support which served as the charge collector of an application type electrode, as shown above, While the phenomenon in which an electrode active material layer exfoliates from electrode support compared with the case where planate electrode support like a punching metal is used is controlled, From it being a metal porous body of a spacial configuration, the electron conductivity over the direction of the thickness of an electrode can improve, therefore high capacity-ization by improvement in the capacity factor of an electrode active material can be attained, and the sag at the time of large current discharging can be controlled further. And by establishing one or more the non-punch stations or application-of-pressure punch stations for current collection in the periphery of a metal porous body in parallel to an undulating direction, extension of an electrode is controlled by the undulating direction of a metal porous body, and the endurance of an electrode improves. Therefore, the application type electrode for cells excellent in cycle life property can be obtained. When it conveys at the undulating direction and right angle of a metal porous body, there is no extension of the electrode itself and there is no modification of the metal porous body which is electrode support. And by establishing a non-punch station or an application-of-pressure punch station in the periphery of a metal porous body, even if it performs conveyance and a roller press in a right angle or which direction of parallel to the undulating direction of a metal porous body, there is no extension of the electrode itself, and there is no modification in the spacial configuration of a metal porous body.

[0014]

[Example]Hereafter, working example of this invention is described.

[0015]Drawing 1 is drawing of longitudinal section showing the example of composition of the metallic mold used for punching of a metal plate or a metallic foil. The bottom part which has much punch 6 with which 5 used the tip as the truncated cone form, and 7 are the punches which established the crevice 8 in the portion corresponding to the punch 6. This punch 6 and crevice 8 have structure which agrees alternately with the upper and the bottom.

[0016]A metal plate or the metallic foil 1 is arranged between besides type 7 and the bottom part 5, and if the punch 7 and the bottom part 5 are pressurized in the direction which approaches relatively, a metal plate or the metallic foil 1 will be punctured, being extended by corrugated form when pushed by the tip of the punch 6 into the crevice 8. A metal porous body as shown in drawing 2 (a) by such punching is obtained. In the figure, 2 is a hole and 3 shows the barricade which was formed up and down at the time of punching as for the pressurizing direction side of a metal plate or the metallic foil 1. t shows the original metal plate or the thickness of the metallic foil 1, and T shows the thickness on appearance including the barricade 3.

[0017]In the metallic mold shown in drawing 1, since the punch 6 and the crevice 8 are moreover established in the up-and-down couple by turns, the barricade 3 is formed in both sides of a metal plate or the metallic foil 1 by punching from the both sides of a metal plate or a metallic foil. If the tip of the lower barricade 3 is connected from the tip of the barricade 3 of the upper part, the model figure of corrugated form structure like top degree drawing 2 (b) can be drawn. Therefore, when waveform constitution is shown, the structure of drawing 2 (a) is meant.

It has indicated to corrugated form especially for simplification.

[0018]The 30-150-micrometer-thick range is suitable for the metal plate or metallic foil used by this invention so that it may mention later, and the size of the hole punched has that preferred whose length of one side it is a like in the diameter of 0.2-2 mm, a rectangle, or it at a circular hole, and is 0.2-2 mm.

[0019]As said metal plate or a metallic foil, the metal plate or foil which covered the metal or the surface of electrolysis solution-proof nature with the metal of electrolysis solution-proof nature is used.

[0020]Therefore, if the thickness of a metal plate or the metallic foil 1 is displayed as t (micrometer) as shown in drawing 2, and thickness of the apparent metal porous body between the barricade tips of those upper and lower sides is set to T (micrometer), it will become important when the value of this ratio T/t chooses a metal porous body.

[0021]Drawing 3 shows, the aperture shape, i.e., the upper surface **** figure, of the metal porous body used by this invention, and shows drawing 4 the conceptual composition of the a-a' vertical section of this metal porous body.

[0022]The composition of the electrode vertical section which made both sides of the corrugated form porous body shown in drawing 2 carry out application formation of an active material or the hydrogen storing metal alloy powder 4 is shown in drawing 5.

[0023]Drawing 6 shows the conventional punching metal, for example, punctures the center-to-center pitch D for the hole 10 with a diameter of 2 mm as 3.5 mm to the 50-micrometer-thick nickel board 9. In this case, even if a barricade is formed around the hole which serves as the form where a metal plate is pierced and cut at punch and the edge of a crevice, using the punch which does not have a tip of a truncated cone form, and is punched in this way, to it, it is only small. Next, more concrete working example is described.

[0024]The 20-160-micrometer-thick nickel board was punched by the specification shown all over Table 1, and the metal porous body was produced. in addition -- making arrangement of a hole into the shape of a lattice -- a hole -- the pitch of a between was 3.5 mm. The pressurizing condition, a transportation direction, and the direction of a roller press are taken into consideration about the process conditions of an electrode, A paste type nickel electrode and a

metal hydride electrode are produced using these metal porous bodies, and the result of having constituted the encapsulated type Ni Cd battery and the same type nickel hydrogen storage battery for 50Ah, and having evaluated the nickel electrode and the metal hydride electrode is described.

[0025]

[Table 1]

電極の種類	金属板(箔)の厚さ t (μm)	金属多孔体見掛け上の厚さ T (μm)	厚さ比率 T/t	穿孔部の形状	開孔率 (%)	加圧前の厚さ比率 S/E	圧縮率 (%)	波形方向と長尺状集電体方向	波形方向に対する搬送方向とローラプレス方向
a	50	800	1.6	略矩形 (-辺2mm)	4.5	1.2	4.0	同方向	直角方向
b	100	1200	1.2		4.5	1.2	4.0	"	"
c	150	2100	1.4		4.5	1.2	4.0	"	"
d	80	1200	1.5	略円形 (径2mm)	3.0	1.0	3.0	"	"
e	100	2000	2.0		4.0	1.5	2.5	"	"
f	60	1980	3.3		5.5	2.0	4.5	"	"
g	30	150	5	略長方形	3.0	1.0	2.5	"	"
h	50	400	8	"	6.0	1.5	4.5	"	"
i	100	1200	1.2	"	4.0	1.2	4.0	"	平行方向
j	80	1600	2.0	"	4.0	1.5	4.0	"	平行方向
k	20	500	2.5	略矩形	4.5	1.2	4.0	"	直角方向
l	160	2240	1.4	"	4.5	1.2	4.0	"	直角方向
m	100	1200	1.2	"	4.0	2.5	4.0	"	"
n	100	1200	1.2	"	4.0	0.8	4.0	"	"
o	80	1200	1.5	"	4.0	1.2	2.0	"	"
p	80	1200	1.5	"	4.0	1.2	5.0	"	"
q	100	1500	1.5	"	4.0	1.2	4.0	直角方向	"
r	100	1500	1.5	"	4.0	2.5	5.5	—	平行方向
s	50	800	1.6	"	2.5	1.2	4.0	同方向	直角方向
t	50	800	1.6	"	6.5	1.2	4.0	"	"
u	パンチングメタル(図6に示す)								
v	100	800	8	略矩形	4.0	1.0	3.0	同方向	直角方向
w	80	1600	2.0	"	4.5	1.1	3.5	"	"
x	50	1500	3.0	"	3.5	1.2	4.0	"	"
y	パンチングメタル(図6に示す)								

[0026][Working example 1] First, to the nickel hydroxide powder 100g, the graphite powder 10g, the nickel powder 5g, the cobalt powder 10g, the 3wt% solution 55g of carboxymethyl cellulose, and 5 g of 48wt% water dispersions of styrene butadiene rubber were kneaded, and it was made paste state. After making the tub which accommodated this paste pass each metal porous body shown in a-t in Table 1 and plastering both sides of a metal porous body with a paste, After passing the slit made from stainless steel and adjusting a paste application object to fixed thickness, after letting the drying process pass, the roller press was performed, and the 0.65-mm-thick application type nickel positive electrode was produced.

[0027]Next, it judged in size of 100 mm x 120 mm by using these nickel electrodes as significant part. In this way, the electrochemical theoretical capacity computed from the amount of nickel hydroxide contained in one electrode obtained is 4.25Ah. It was referred to as 55Ah, using this electrode 13 sheets. Capacity of the cadmium negative electrode was set to 6.7Ah per sheet, and was considered as the composition using this electrode 14 sheets.

[0028]As the metal porous body used here is shown in drawing 7, drawing 8, and drawing 9, the non-punch station or application-of-pressure punch station for current collection is provided in parallel to the undulating direction (it expresses as the schematic illustration of the shape shown in drawing 2) of the corrugated form metal porous body 11. And it provides in long shape and the lead board 13 is attached to this portion at the periphery of the corrugated form metal porous body. Drawing 7 (a) is the example in which drawing 7 (b) provided the collecting section which constitutes a non-punch station or an application-of-pressure punch station in the upper part of the electrode again at both the upper part and the lower part. It is the composition which controlled that an electrode elongated all to an undulating direction.

[0029]Drawing 8 is a case where the collecting section is provided in the both sides of an electrode. Drawing 9 is the example which provided the collecting section in a part of electrode around top, and attached the lead board 13 to this portion. The undulating direction of the metal porous body is located in a line with the horizontal horizontal direction of the electrode so that an electrode may not develop from a transverse direction to a lengthwise direction. By using such an electrode configuration, extension of a lengthwise direction becomes less than a transverse direction at least. If an electrode is extended to a lengthwise direction, a short pass will be generated in the lower part of an electrode. The extension to a transverse direction controls this short pass, and leads to extension of a cycle life.

[0030]If it carries out from this viewpoint, although a long shape collecting section is not parallel to the undulating direction of a metal porous body, it can control to some extent by providing a collecting section in the both sides of an electrode, and fixing the extension to a transverse direction with the lead board 13, as shown in drawing 10. There is also little extension to a lengthwise direction. However, since drawing 11 has a long shape collecting section in the undulating direction and right angle of a metal porous body and an undulating direction is moreover located to the mounting directions of an electrode in a lengthwise direction, an electrode is extended to a lengthwise direction, and a cycle life becomes short. This electrode configuration is not preferred from a battery characteristic.

[0031]The encapsulated type nickel-Cd cell of the square shape of nominal capacity 50Ah was constituted combining the separator which consists of a nonwoven fabric of these nickel positive electrodes, a publicly known cadmium negative electrode, and the product made of polyamide resin. A proper quantity of 31wt% solution of the potassium hydrate in which 30 g/l of lithium hydroxide was dissolved was used for the electrolysis solution. In this way, cell A-J using the nickel positive electrode obtained from metal porous body a-j shown in Table 1 was produced.

[0032]Make shape of the punch station of a metal porous body into an approximately rectangle, circular, and a rectangle here, and, as for the case of rectangular directions, a transportation direction and the direction of a roller press do not have involvement in the

existence of the non-punch station for reinforcement, or an application-of-pressure punch station to the undulating direction of a metal porous body, It is a case where the non-punch station or application-of-pressure punch station for reinforcement is established in a periphery only about the case of being parallel.

[0033]The structure of the square-shaped alkaline battery for 50Ah carried out here is shown in drawing 12. in drawing 12 -- 14 -- a cadmium negative electrode and 15 -- as for a negative pole terminal and 19, a separator and 17 are [a safety valve and 21] the lids of a battery case a positive pole terminal and 20 a battery case and 18 a nickel positive electrode and 16. The shape of the punch station of a metal porous body was used by this example, as shown in drawing 13, and also various punching is possible for it.

[0034]The cell constituted from above conditions is charged by 0.1C for 15 hours, it discharges until cell voltage amounts to 1.0V after [0.2C] the pause of 1 hour, and it is this condition, and is 3 cycle *****. Subsequently, discharge of 0.5C and 5 cycle eye was similarly set [the charge condition] to 1C for discharge of the four-cycle eye, and the discharge characteristic was compared. The cycle-life examination to which cell voltage charges by 0.3C and carries out 4 hours and discharge to 1V by 0.5C was done after 6 cycle eye, and it compared the constituent conditions and cycle life property of the nickel positive electrode. These results are shown in Table 2.

[0035]

[Table 2]

電池 種類	正極理論 容量 (Ah)	3サイクル目 利用率 (%) 0.2C放電	放電電流 0.5C/0.2C 容量比率 (%)	放電電流 1C/0.2C 容量比率 (%)	200サイクル目 利用率 (%) 0.2C放電	500サイクル目 利用率 (%) 0.2C放電
A	55.2	92.0	93.0	91.5	91.0	89.8
B	56.3	94.2	94.5	92.0	93.1	90.8
C	55.1	96.5	95.2	92.3	94.8	93.5
D	55.4	93.5	94.0	93.1	92.2	90.2
E	55.8	94.8	93.5	90.5	88.3	85.5
F	55.5	90.5	85.5	80.2	85.3	83.5
G	55.7	91.8	93.0	92.2	86.4	84.2
H	55.0	90.5	91.5	90.1	88.0	85.4
I	55.2	94.3	94.5	92.2	91.5	90.0
J	55.4	93.0	93.6	91.5	91.1	89.5

[0036]Thickness and hole density with a metal plate (foil) and a metal porous body apparent on the other hand, the rate (S/E) of a thickness ratio before application of pressure, Although the existence of the undulating direction of a metal porous body, the direction of a long shape collecting section and the transportation direction to the undulating direction of a metal porous body, the direction of a roller press and the non-punch station for current collection, or an application-of-pressure punch station, etc. are the ranges of this invention, when it separates from the optimal range, the example to which a battery characteristic falls is shown in Table 3.

[0037]

[Table 3]

電池種類	正極理論容量 (Ah)	3444項目利用率 (%) 0.2C放電	放電電流 0.5C/0.2C 容量比率 (%)	放電電流 1C/0.2C 容量比率 (%)	充、放電サイクル寿命 (回)	電池劣化原因
K	55.8	85.0	82.1	74.1	150	脱落現象 (剥離)
L	56.5	89.0	85.0	83.0	250	抵抗増大 (膨張)
M	55.4	80.5	73.5	60.4	200	脱落現象 (膨張)
N	56.0	94.8	93.5	87.0	255	短絡現象
O	55.0	91.3	89.4	83.2	270	強度弱く脱落現象
P	54.8	80.2	75.0	70.5	200	電極破壊
Q	55.8	85.8	81.3	75.5	240	短絡現象 (電極伸長)
R	破壊	—	—	—	—	—
S	56.2	80.5	75.6	70.2	150	脱落、剥離現象
T	55.3	85.0	80.5	75.4	300	抵抗増加
U	56.5	91.5	85.3	75.0	130	脱落現象

[0038]The cells K and L the thickness of a metal plate (foil), the apparent thickness of a metal porous body, and the cells M and N The rate (S/E) of a thickness ratio before application of pressure, When an application-of-pressure rate is unsuitable, the undulating direction of a metal porous body and the direction of the non-punch station for current collection (application-of-pressure punch station) of the cell Q are rectangular directions and a transportation direction and the direction of a roller press are parallel, the cells S and T of the cells O and P are when hole density is unsuitable. [as opposed to an undulating direction in the cell R] The cell V is a case where the punching metal of a conventional type is used.

[0039]By various cells, the capacity factor of the nickel hydroxide used for the nickel electrode in cell A-J in this example is 90.5 to 96.5%, and holds not less than 90% which is a practically required capacity factor altogether. Also in a high rate discharging characteristic (the rates 0.5C/0.2C of a capacity factor, 1C/0.2C), 90.5 to 95.2% (not less than 85% reservation) and 85.2 to 93.0% (not less than 80% reservation) are maintained respectively. In a charge-and-discharge cycle test, the service capacity capacity factor of a 200 cycle eye and a 500 cycle eye holds 85.3 to 94.8%, and 83.5 to 93.5% respectively. The practically desirable battery characteristic is shown in this range. As a result of examining about cell K-T shown in Table 3 as one example of the cell to which relevant conditions are not equal in this example on the other hand, the capacity factor of the nickel hydroxide used for the nickel electrode is among 80.2 to 94.8%, and has produced the big difference by the electrode configuration or process conditions. There is also a cell which has not secured practically desirable not less than 90%. Also in the rate of a capacity factor of 0.5C/0.2C and 1C/0.2C which is one of the high rate discharging characteristics, the cell which are 73.5 to 91.5% and 70.5 to 87.0% respectively, produces a big difference similarly and has not secured practically desirable 85% and not less than 80% also exists. The charge-and-discharge cycle life of this seed cell is also among 150 to 300 times, and it is falling substantially compared with cell A-J. There is almost no cell which has attained the cycle life (not less than 60% as capacitance retention) to 500 cycles, The cause has increase of battery internal resistance, and too large electrode thickness, and is

based on poor generating at the time of the capacity lowering by the shortage of collecting capacity, the short circuit in a cell, the electrode destruction by expansion by charge and discharge, exfoliation of an active material, omission, or battery construction (destruction). It turns out that the conventional-type cell (punching metal use) V has the shortest cycle life. Thus, as compared with cell A-J, a battery characteristic falls by battery construction conditions. Therefore, even if it uses the same corrugated form metal porous body, it will turn out that there are desirable electrode configuration conditions and process conditions.

[0040]Although the early capacity factor of the cell U which uses the punching metal of a conventional type for electrode support is as practically equal as the metal porous body of this invention, a big difference is accepted about a high rate discharging characteristic and a cycle life. At 1C / rate of a 0.2C capacity factor, the conventional-type cell U is about 75% to not less than 90% as average value of cell A-J of this example. Also in a cycle life, the adhesion of an active material and a punching metal is bad, and a fall is looked at by service capacity with omission and an exfoliation phenomenon.

[0041]When a metal plate (foil) is processed into the metal porous body of a three-dimensional structure (corrugated form structure) of having a barricade to the circumference of a hole, like this invention by this result, The range of $4 \leq T/t \leq 40$ (however, $600 \leq T$ (micrometer) ≤ 2100 , $30 \leq t$ (micrometer) ≤ 150) has the most practical ratio of apparent thickness T (micrometer) including a barricade, and thickness t (micrometer) of the original metal plate (foil). This expression of relations is shown in drawing 14. It is a range with a practically desirable portion currently surrounded by the figure inner substance line.

[0042]Where an active material is applied, in a ratio with electrode thickness [before application of pressure] S (mm), the range of $1.0 \leq S/E \leq 2.0$ can apply to apparent thickness [of a corrugated form metal porous body] E (mm), and its both sides practically. Rate of thickness ratio S / E value before electrode application of pressure, and the relation of a high rate discharging characteristic are shown in drawing 15 as one example in case the thickness of the electrode substrate at the time of 35% compression is 0.65-1.3 mm. In this case, although the compression ratio was made into 35%, that compression ratio (thickness before thickness/application of pressure after 1-application of pressure) $\times 100\%$ shows the relation of the intermediate terminal voltage at the time of a display and discharge to drawing 16.

[0043]25 to 45% of a compression ratio can be said to be the range for which it was most suitable practically from an experimental result as shown in Tables 2 and 3. When both contact resistance is large when it is greatly related to the adhesion of an active material and a metal porous body and this value is small, and this value is too large, electrode strength is weak, and collecting capacity also becomes scarce and that of the hole density of a corrugated form metal porous body is not preferred practically. Then, the hole density of the capacity factor of an active material, a cycle life, etc. to a metal porous body has 30 to 60% of desirable range.

This relation is as being shown in drawing 17.

[0044]If T/t is less than four also in drawing 14, the apparent thickness of the spacial configuration of a metal porous body is small, and there is no great difference as compared with the cheap punching metal of a conventional type. On the other hand, if T/t exceeds 40, manufacture of a corrugated form metal porous body becomes difficult, and is not practical from productivity. In drawing 15, if S/E is less than 1.0, the degree which generates a short pass in the barricade on the surface of a metal porous body becomes high, and is unsuitable from the field of reliability. On the other hand, if 2.0 is exceeded, the electrode itself will become thick, the corrugated form network of a metal porous body does not spread in the whole, but the collecting capacity of the electrode itself declines. About the compression ratio of drawing 16, if it is less than 25%, the adhesion of an active material and a corrugated form metal porous body is insufficient, moreover, electrode strength will also be weak, and a high rate discharging characteristic will also worsen, and a cycle life will also become short. On the other hand, if 45% is exceeded, the electrode itself will be pressurized too much, and it becomes low porosity with structure destruction of a corrugated form metal porous body, and an active material does not act enough, but the problem that the endurance as an electrode is missing is generated.

[0045]Thus, if relevant conditions are chosen and an electrode and a cell are constituted, the electron conductivity over the direction of thickness will be secured and the service capacity fall in large current discharging will be considered that were few and reinforcement was attained.

[0046]As construction material of a corrugated form metal porous body, alkali-proof metal is preferred, and the thing of composition of having plated with one or more sorts of nickel, cobalt, copper, and zinc to nickel, the nickel alloy, or the iron base is good.

[0047]Although this corrugated form metal porous body is making the barricade form in the circumference of a punch station, since a pressurizing process is applied at the time of electrode manufacture, the tip part of the barricade of the metal porous body in the inside of the application layer of an electrode is crooked, and an inter-electrode short circuit is prevented. Therefore, when a pressurizing process is applied, it is satisfactory, but if the barricade (projection) tip of the metal porous body is crooked beforehand, the reliability in connection with a short pass will improve further. The structure of the corrugated form metal porous body at this time is shown in drawing 18 (a) and (b). 22 in a figure shows the flection at the tip of a barricade.

[0048]By puncturing a metal plate (foil) and using the metal porous body of the spacial configuration in which the barricade was made to form intentionally by the above result, as electrode support of the corrugated form which constitutes an application type nickel electrode, While improving the electron conductivity of an electrode, the exfoliation phenomenon of an

active material layer can be controlled, and the cell which was excellent in a discharge characteristic and cycle life property can be constituted. Although an effect is accepted even from one side of a metal plate, since the portion from which the direction punched from both sides serves as a skeleton of an electrode is arranged in the center, a perforating direction becomes advantageous to a battery characteristic. About the size of the hole by which the opening was carried out, when it is made small, compared with the thickness of the original metal plate, thickness on appearance cannot become large easily and the effect of this invention becomes small. conversely, the hole which adjoins when it enlarges -- the distance of a between becoming long, and the degree which contributes to the improvement in electronic conductivity becoming small, and, Furthermore the fall of the holding power of an electrode active material will be caused, and when circular, in the case of 0.2-2 mm, a rectangle, or shape similar to this, the diameter was understood that the effect of this invention is large when a length of one side was made into the range of 0.2-2 mm.

[0049]This invention is compared with a punching metal planate as electrode support in the case of constituting an application type nickel electrode above like, It becomes possible to raise a battery characteristic, and compared with the letter nickel porous body of foaming which moreover has the three-dimensional structure generally, the thing which processed fibrous nickel in the shape of felt, etc., it can produce cheaply to about 1 / three to 1/5, and cheap-ization of electrode cost is attained. Although the application type nickel electrode was indicated in working example, The zinc electrode and cadmium electrode in which other application type electrodes are possible, an iron electrode, etc., Or the lead oxide electrode for lead storage batteries, the lithium multiple oxide electrode and carbon electrodes of a lithium secondary battery, The corrugated form metal porous body of this invention can be used for the place currently used as electrode support (charge collector), such as a punching metal, an expanded metal, a lattice and metal nets, such as carbon electrodes, the Russ board, a letter of foaming, or a fibrous porous body of an air-zinc carbon cell. It is suitable for the cell made into the shape of an angle template which prevents especially extension of an electrode.

[Working example 2] A metal plate or a metallic foil is made to punch from both sides by the same method as working example 1, After producing the metal porous body of the corrugated form which formed the barricade intentionally and plastering both sides of the metal porous body of this corrugated form with the pace of a hydrogen storing metal alloy, After passing the slit made from stainless steel and adjusting a paste application object to fixed thickness, after letting the drying process pass, the roller press was performed, and the 0.50-mm-thick application type hydrogen storing metal alloy negative electrode was created.

[0050]Next, it judged in the size with a usable area of 100 mm x 120 mm as these hydrogen storing metal alloy electrodes. In this way, electrochemical service capacity computed from the amount of hydrogen storing metal alloys contained in the negative electrode obtained was set

to 6.7Ah per sheet, used 14 sheets of this electrode plate, and set it to 94Ah.

[0051]The metal porous body used here is made into long shape in the undulating direction of the corrugated form metal porous body 11, as shown in drawing 7 of working example 1, and drawing 8, and it has provided the non-punch station or the application-of-pressure punch station 12 for current collection in parallel to this direction. And the square-shaped nickel hydride battery as shown in drawing 12 was constituted.

[0052]The square-shaped alkaline battery of nominal capacity 50Ah was constituted combining the separator which consists of the publicly known sintering mold nickel positive electrode and polyamide resin the life-span of [polyamide resin] can be extended comparatively so that the characteristic of these hydrogen storing metal alloy negative electrodes and negative electrodes may be known. Therefore, battery construction and a test method are almost the same as working example 1 except having used the hydrogen storing metal alloy electrode instead of the cadmium electrode as a negative electrode plate. In this way, the cells V and W using the hydrogen storing metal alloy negative electrode obtained from the metal porous body v, w, and x shown in Table 1 and X were produced. These results are shown in Table 4.

[0053]

[Table 4]

電池 種類	電池公称 容量 (Ah)	3#以外目 放電容量 0.2C放電 (Ah)	放電電流 1C/0.2C 容量比率 (%)	放電電流 2C/0.2C 容量比率 (%)	500#以外目 放電容量 0.2C放電 (Ah)	1000#以外目 放電容量 0.2C放電 (Ah)
V	50	51.5	92.2	80.6	50.2	48.5
W	50	51.0	92.7	80.4	50.5	49.0
X	50	52.0	90.6	80.0	51.3	49.5
Y	50	50.5	84.2	74.3	45.0	40.5

[0054]Here, shape of the punch station of a metal porous body was made into the approximately rectangle, and tried the examination about the case where a transportation direction and the direction of a roller press are made into rectangular directions to the undulating direction of a metal porous body. the $\text{MmNi}_{3.6}\text{Co}_{0.7}\text{Mn}_{0.4}\text{aluminum}_{0.3}$ system generally released as a presentation of the used hydrogen storing metal alloy -- the alloy was used. The nickel positive electrode used the sintering mold electrode which was excellent in the cycle life so that negative-electrode performance could be distinguished.

[0055]The capacity of the hydrogen storing metal alloy used for the negative electrode in the cells V and W and X in this example constitutes a cell from 230 or more mAh/g, and real service capacity is regulated by the capacity of a sintering mold anode. Therefore, initial capacity is as practically equal as the conventional-type cell Y. However, if a discharge current value becomes large with 1C and 2C, the difference is produced in the metal porous body of this invention, and the punching metal of the conventional type. When it becomes high rate discharge, by the cell of this invention at the time of the rates 1C/0.2C of a capacity factor, and

2C/0.2C. By the cell of a conventional type, it is falling about 26% 16% with 84.2% and 74.3% respectively to 90.6 to 92.7%, and 80.0 to 80.6% at the time of the rates 1C/0.2C of a capacity factor, and 2C/0.2C. Although the service capacity of a 500 cycle eye and a 1000 cycle eye is not as the anode of working example 1, either, it is falling greatly. As this cause, the direction of the conventional-type cell is inferior in the electron conductivity to a thickness direction, and resistance between a punching metal and a hydrogen storing metal alloy is considered that were large and collecting capacity became low. By the cell of this invention, a current collection operation works between a hydrogen storing metal alloy and a corrugated form metal porous body, and there are little capacity lowering and sag. Thus, by providing the non-punch station or application-of-pressure punch station for current collection in parallel to the undulating direction of a corrugated form metal porous body, there are also no troubles, such as extension of a metal porous body and a crack, and the nickel hydride battery excellent in endurance and productivity can be produced.

[Working example 3] The application type electrode for cells which forms the application layer of an active material or hydrogen storing metal alloy powder in both sides of a corrugated form metal porous body was manufactured as follows as one of the examples of manufacture. First, as a metal porous body band-like [long], a metal plate or a metallic foil is punched from both sides, that punched hole -- what was formed in corrugated form was prepared, the this long picture band-like metal porous body was conveyed to a parallel direction or rectangular directions to that undulating direction, and an active material or hydrogen storing metal alloy powder was made to apply in the barricade formed in the circumference The example conveyed to rectangular directions to the undulating direction of a metal porous body is shown in drawing 19 (a). The example which provides and conveys a non-punch station or an application-of-pressure punch station to the both-sides periphery of a metal porous body is shown in drawing 19 (b). It is better to provide a non-punch station or an application-of-pressure punch station like drawing 19 (b), when conveying especially to the undulating direction and parallel direction of a metal porous body. If it conveys with such a structure, there is also no process top trouble and homogeneous thickness can be plastered with an active material or hydrogen storing metal alloy powder.

[Working example 4] Both sides of the corrugated form metal porous body were plastered with an active material or hydrogen storing metal alloy powder, and the metal porous body constituted long band-like one or in the shape of short length was used as a method of manufacturing the application type electrode for cells. the metal porous body punches a metal plate or a metallic foil from both sides -- the punched hole -- it having been formed in corrugated form of the barricade formed in the circumference, and, Both sides of the metal plate or metallic foil punched at this corrugated form were equipped with the application layer which consists of an active material or hydrogen storing metal alloy powder, it conveyed to

rectangular directions to the undulating direction of this metal porous body, and the roller press or the embossing roller press whose surface of a roller is uneven shape was performed once or more. The composition is shown in drawing 20 (a) and (b). drawing 20 (a) is a case where conveyed to rectangular directions to the undulating direction of a metal porous body, and a roller press is performed once or more -- again, Drawing 20 (b) is a case where provided and conveyed the same non-punch station or application-of-pressure punch station for reinforcement to the both-sides periphery of a metal porous body, and an embossing roller press is performed once or more. When establishing the non-punch station or application-of-pressure punch station for reinforcement in the periphery of a metal porous body, it may convey in parallel to the corrugated form direction of a metal porous body, and a roller press may be performed. The metal porous body without a reinforcement section is greatly elongated at the time of 1 times or more of a roller press, the spacial configuration of corrugated form decreases, apparent thickness decreases, and an electrode characteristic falls remarkably. [0056] Thus, to the long band electrode board which made the application layer of an active material or hydrogen storing metal alloy powder form in both sides of a long shape metal porous body, to the undulating direction of a metal porous body, in parallel, it cut so that that parallel direction might moreover be on the direction side of a long picture, and the electrode was manufactured as shown in drawing 21 (a) and (b). And although it is more desirable to provide the non-punch station or application-of-pressure punch station for current collection in parallel to the undulating direction like drawing 21 (b), the method of drawing 21 (a) which establishes the non-punch station or application-of-pressure punch station for current collection in both sides to an undulating direction in rectangular directions at both sides may be used. Drawing 21 is one of them, and its case where it has the non-punch station and application-of-pressure punch station for reinforcement in the periphery of a corrugated form metal porous body is preferred, and it can fix a lead board by making this portion current collection.

[Working example 5] It carried out about two kinds as a method of plastering both sides of a corrugated form metal porous body with paste state active material or hydrogen storing metal alloy powder. One is a case where it conveys and plasters downward from on the method of conveying and applying a corrugated form metal porous body upwards from the bottom.

[0057] As one of working example, it conveyed in parallel to the undulating direction of a long strip metal porous body. The metal porous body established the non-punch station or the application-of-pressure punch station in reinforcement band-like at the periphery.

[0058] First, as shown in drawing 22, the metal porous body 11 which formed the non-punch station 12 for reinforcement with the rollers 23, 24, and 25 for conveyance was conveyed to the corrugated form direction and parallel. An application layer is formed in both sides of through and the metal porous body 11 for the inside of the container 29 having a paste state

active material or the hydrogen storing metal alloy powder 4, and the inside of the dryer 27 was passed, adjusting thickness to the slit 26. The metal porous body which furthermore has an application layer pressurized suitable thickness with the roller press. 28 is a jig for meandering prevention.

[0059]As following working example, it conveyed right-angled to the undulating direction of a long strip metal porous body. The non-punch station or the application-of-pressure punch station was established in reinforcement of the metal porous body band-like at the periphery. As shown in drawing 23, the metal porous body 11 which formed the non-punch station 12 for reinforcement with the rollers 23, 24, and 25 for conveyance was conveyed at the corrugated form direction and the right angle. An application layer is formed in both sides of through and the metal porous body 11 for the inside of the container 29 having a paste state active material or the hydrogen storing metal alloy powder 4, and the inside of the dryer 27 was passed, adjusting thickness to the slit 26. Furthermore, the thickness of the electrode body was controlled by the thickness tester 30. This was detected and the metal porous body which has an application layer was pressurized with the embossing roller press at suitable thickness.

[0060]The battery characteristic using the corrugated form metal porous body of this invention is superior to the cell which used the punching metal of the conventional type. It becomes cheaper than the nickel electrode which filled up the sintering type nickel electrode and the latter nickel porous body of foaming with the electrode active material as a nickel positive electrode from this thing. Therefore, this invention has the feature which can produce cheaply the material which constitutes an electrode, especially the metal porous body which is electrode support. In the process which constitutes a cell from an electrode, it excels also in endurance and productivity, and mass production nature.

[0061]

[Effect of the Invention]punching a metal plate or a metallic foil from both sides by this invention as mentioned above -- the punched hole -- the corrugated form metal porous body formed in corrugated form of the barricade formed in the circumference is used.

Therefore, the exfoliation phenomenon of an electrode can be controlled and the electron conductivity over a thickness direction can be improved.

Thereby, improvement in a high rate discharging characteristic and cycle life property is attained. By establishing the non-punch station for current collection, or an application-of-pressure punch station in the undulating direction and parallel direction of a corrugated form metal porous body, there is no extension of an electrode, and it excels in endurance, and there is no extension of an electrode into conveyance and a roller press, there is also no generating of inferior goods, and it can manufacture efficiently. Cheap-ization of electrode cost can be attained by obtaining the battery characteristic superior to the conventional punching metal from the sintering type electrode and foaming metal type electrode which are used now. And it

excels in productivity and mass production nature, and man day cost can also be reduced.

[Translation done.]